VINYL COPOLYMERS

BY
GLENWOOD LOUIS SCHERTZ
B.S., University of Illinois, 1934
M.S., University of Illinois, 1938

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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Introduction

The copolymerization of two monomers has been represented with two unimolecular rate equations.[1] By means of interrupted polymerizations the ratio of the two rate constants can be determined. In this laboratory[2] this ratio has been determined for vinyl chloride and vinyl acetate and found to be in the range 1.5 to 2.0. The suggestion has been made that since vinyl chloride enters the copolymer more rapidly than vinyl acetate, the vinyl chloride-acetate copolymer must be heterogeneous in composition. The purpose of this investigation was to study the composition of vinyl chloride-acetate copolymers and to apply the method of interrupted copolymerizations to the study of copolymers of *p*-chlorostyrene.

Discussion of Results

Polyvinyl acetate, polyvinyl chloride, and a vinyl chloride-acetate copolymer have been mixed and then separated into three fractions approximately equal in quantity and composition to the original polymers. 1-Heptyne was used to extract polyvinyl acetate. The copolymer was extracted with phenylacetylene and the polyvinyl chloride was obtained as the insoluble fraction. When this method of fractionation was applied to various polymers obtained by polymerization of mixtures of vinyl chloride and vinyl acetate no polyvinyl chloride or polyvinyl acetate was obtained; hence neither of these two monomers polymerizes alone in the mixture.

The heterogeneous composition of vinyl chloride-acetate copolymers has been demonstrated by extracting these copolymers with l-heptyne and phenylacetylene. Copolymers were separated into fractions both higher and lower in vinyl chloride content than the original sample.

The method of interrupted polymerization of mixtures of *p*-chlorostyrene and methyl methacrylate has been used to de-

termine the ratio of the rate constants. The value 1.5 shows that the chlorostyrene enters the copolymer more rapidly than the methacrylate; however, when the two monomers were each polymerized alone the methacrylate was found to polymerize more rapidly than the chlorostyrene. The ratio of the two rate constants was found to remain the same for polymerizations in bulk from 40° to 120°, either with or without ultraviolet light, and in the solvents dioxane, methyl alcohol, and acetone.

Interrupted polymerizations of mixtures of *p*-chlorostyrene and styrene were used to determine the activating effect of the chlorine atom. The substituted styrene entered the copolymer more rapidly than the styrene. The rates of polymerization of the *meta* and *para* isomers were compared by polymerizing each with methyl methacrylate. No difference between these two isomers was observed.

The molecular weights of chlorostyrene-methyl methacrylate copolymers as measured by viscosity were found to be unaffected by the degree of conversion when comparisons were made over a range of 9 to 62 per cent yields of polymers.

When mixtures of *p*-chlorostyrene and vinyl acetate were polymerized low yields were obtained. Chlorine analyses indicated that these polymers contained more than 91 per cent chlorostyrene.

The specific rotation of the *l*-menthyl acrylate unit in poly-*l*-menthyl acrylate[3] has been found to differ slightly from the specific rotation of this unit in the *l*-menthl acrylate-*p*-chlorostyrene copolymer. A similar difference was observed for poly-*d*-*s*-butyl methacrylate and the corresponding copolymer with *p*-chlorostyrene.

References

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2. Jones, Thesis, Doctor of Philosophy, University of Illinois, 1942.
3. Marvel, Dec, and Cooke, J. Am. Chem. Soc., **62**, 3499 (1940).

VITA

The writer was born at Roanoke, Illinois, September 11, 1911. He graduated from Metamora Township High School. After two years of study at Goshen College he transferred to the University of Illinois where he received the B. S. degree in 1934 and M. S. degree in 1938.

During the years 1932-1940 he taught in the public schools of Illinois and returned to the University of Illinois in 1940 where he was a teaching assistant from 1941 to 1942 and received the Monsanto Fellowship for 1942-1943.

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